

APPENDIX A

Detailed Description of In Situ Methods

Methods currently available for in situ measurement of total dissolved gas pressure include the gas saturometer and the gas tensionometer. These are theoretically the same instrument but differ in the nature of the pressure measuring device. A detailed description of each method including a reference to the original work, a description of the equipment needed, a short discussion of the analytical principle used, an example of the calculations required, and any specific information on precision, interference, advantages, disadvantages, etc. are given below.

1. Gas Saturometer (Weiss). The gas saturometer is a relatively inexpensive, field portable device which measures the total gas pressure directly. The device consists of a metal framework upon which is wound about 100 feet of silastic tubing. This tubing is permeable to all gases but not to liquid water. When this device is submerged, the gases in the water equilibrate with the volume of gas present in the tubing and the total dissolved gas pressure in solution is read on a pressure gauge. This pressure includes the contribution of water vapor pressure (P_v). The gauge reads positive pressure for supersaturated waters and negative pressures for undersaturated waters. The gauge reads the sum of the partial pressures all gases present in solution including nitrogen, oxygen, argon, carbon dioxide (usually very low) and water vapor and measures it relative to atmospheric pressure. Thus it is necessary to know the atmospheric pressure at the time of the measurement and also the water temperature. The total relative saturation is calculated by the following equation:

$$\frac{P_B + \Delta P}{P_B} \times 100 = \text{Total Gas Saturation}$$

where P_B is the atmospheric pressure in torr (mm Hg)

and P is the saturometer reading in torr.

Thus the percent saturation obtained is relative to existing atmospheric pressure at the site and the water surface, no matter at what depth the device is placed.

Determination of the nitrogen supersaturation (nitrogen + argon) requires, in addition to the measurement of total gas pressure, a separate measurement of dissolved oxygen concentration. This can be obtained by either the standard Winkler technique or with a calibrated dissolved oxygen probe.

Having measured the dissolved oxygen concentrations along with total gas pressure, the following calculations can be used to obtain dissolved nitrogen saturation.

Percent oxygen saturation is determined by converting the measured concentration of dissolved oxygen in mg/l to ml/l and then dividing by the saturation concentration at the measured water temperature which can be obtained from Table D-1. The formula for this calculation is shown below:

$$\text{Percent } O_2 \text{ saturation} = \frac{O_2 \text{ measured (mg/l)} (0.70 \text{ ml/mg}) (100)}{O_2 \text{ saturation (ml/l) at measured H}_2\text{O temp \& pressure}}$$

The conversion factor 0.70 ml/mg is the reciprocal of the density of gaseous oxygen at 0°C and 760 torr (STP). The percent nitrogen (including argon) is then obtained as follows (Nebeker 1976):

$$\text{Step (1) } P(O_2) = O_2 \text{ (mg/l)} \frac{(0.70 \text{ ml/mg})}{B(O_2)/1 \text{ atmosphere}} \times (0.76 \text{ torr/(atmosphere} \times \text{ml)})$$

$$\text{Step (2) } P(N_2) = P_B + \Delta P - (P(O_2) + P_v)$$

$$\text{Step (3) Percent } N_2 = \frac{P(N_2)}{0.79 (P_B - P_v)} \times 100$$

where $P(O_2)$ = oxygen pressure (torr)

$B(O_2)$ = Bunsen coefficient for oxygen (1/1 atmosphere), table D-5

$$0.76 = 760 \text{ (torr/atmosphere)} \times \frac{1}{1000 \text{ ml}}$$

$P(N_2)$ = nitrogen pressure (torr), including Argon

P_B = barometric pressure (torr)

ΔP = satumeter reading (torr)

P_v = water vapor pressure (torr), table D-4

0.79 = Percent N_2 + Ar in dry air

The final result, percent N, is the percent nitrogen saturation (including argon).

A detailed description of the procedure to use the saturometer is given below.

After arrival on site, the protective cover is removed and the membrane sensor immersed in the water to a depth of one foot. The sensor is shaken vigorously throughout the measuring period to dislodge bubbles which tend to cling to the membrane and cause artificially low results. For those saturometers equipped with a jet pump, the use of this device should reduce the amount of shaking required. Equilibrium will generally be achieved within 15 minutes but for highly supersaturated water, it may take somewhat longer. When the gauge does not show a change for a minute, the equilibrium point has been reached. The pressure reading obtained at equilibrium is recorded as a measure of total dissolved gas pressure difference (P) and used in calculations presented earlier.

The major sources of error associated with use of the saturometer for gas saturation measurements are (a) high pressure leaks, (b) condensation of water inside the silastic tubing and (c) gas bubbles clinging to the outside of the tubing. The symptom of the high pressure leak is a topping out of all readings, or erratic behavior of the pressure gauge, and length of time required for the system to equilibrate. In other words, many readings will be found at a given P, but none above this value. To locate the source of leakage, the tubing is pressurized and inspected visually in much the same manner as used to find leaks in innertubes.

To minimize condensation problems, the saturometer should be dried periodically by placing the device in an electric oven at 80°C for one hour and storing in an area of low humidity.

The clinging of gas bubbles to the outside of the tubing is a problem since the final reading will be representative of an unknown degree of equilibration with the bubbles as well as the dissolved gas. This will result in artificially low readings. In order to minimize this problem, the saturometer must be shaken vigorously throughout the measurement. This is difficult because of the time required to reach equilibrium (generally about 15 minutes). Unless the analyst is patient, readings below the correct values will be reported. The newer models of the saturometer have a manually operated water-jet pump. This pump is used under supersaturated conditions to dislodge bubbles and may reduce the time for the system to come to equilibrium.

2. Gas Tensionometer (D'Aoust). The principle of operation of the gas tensionometer is identical to that of the Weiss saturometer. In this system the pressure gauge has been replaced by a pressure transducer and the size of the device has been reduced markedly (D'Aoust et al., 1976). The measurement technique is also similar and, because of its lower dead space, the time required to reach equilibrium has been reduced. This device is capable of measuring the total gas pressure at depth whereas the Weiss instrument can only be used for surface measurements.

The gas tensionometer reads the absolute gas pressure whether in the water or air. Thus the total dissolved gas pressure is read no matter at what depth the device is placed. The tensionometer can also be used to measure water temperature and atmospheric pressure.

This device is quite easy to use and operator error associated with the satumeter should be reduced with this device. It is also capable of being connected to a recording device to allow continuous monitoring at a single site or interfaced with a remote data collection system.

To calculate total gas saturation, the dissolved gas pressure (in torr) is taken from the digital output of the device, divided by the measured atmospheric pressure (in torr), which is the reading at the surface before immersion, and the resultant multiplied by 100. This value is the total gas saturation. Delta P (ΔP), total gas pressure minus barometric pressure, is from a physical stand-point the more relevant parameter.

To obtain the nitrogen saturation, calculations are identical to that presented for the satumeter (Appendix A-1), and require measurement of O_2 .

The operation of the device is as follows. The device is unpacked and the battery voltage checked to insure sufficient power for operation. The atmospheric pressure (in torr) is obtained by taking a reading with the device before the probe is immersed in water. The probe is placed in the water to a depth of about 10 feet. This insures that bubble formation will not occur on the outside of the tubing even in highly supersaturated water. The probe is allowed to come to equilibrium with the gas dissolved in the water and a reading taken. An equilibrium condition has been established when the digital reading does not change for a minute or more. This usually takes about 10 minutes, but the length of time depends on the temperature and stirring rate. The water temperature is also recorded to enable subtraction of water vapor pressure and calculation of nitrogen saturation.

The major potential problems observed thus far with the gas tensionometer are the calibration of the temperature sensor and the development of high pressure leaks. The temperature sensor should be checked versus a calibrated thermometer before each trip to the field and adjustments made per manufacturer instructions. The development of high pressure leaks can be checked by pressurizing the sensor with syringe injections at the vent cock and observing the stability of the pressure reading, or immersing under water while pressurized and checking for a point source of bubbles.